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### ANNUAL REPORT

## FRACTURE SURFACE ANALYSIS IN COMPOSITE AND TITANIUM BONDING

BY

T. A. DeVILBISS AND J. P. WIGHTMAN

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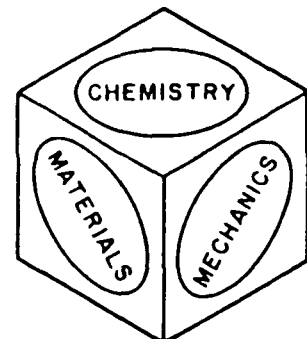
VIRGINIA POLYTECHNIC INSTITUTE  
AND STATE UNIVERSITY

216 NORRIS HALL  
BLACKSBURG, VIRGINIA 24061

Telephone: (703) 961-6824

Telex: 7108753699

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FRACTURE SURFACE ANALYSIS IN COMPOSITE  
AND TITANIUM BONDING

BY  
T. A. DeVILBISS AND J. P. WIGHTMAN

PREPARED FOR  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA - LANGLEY RESEARCH CENTER  
MATERIALS DIVISION  
HAMPTON, VA 23665  
D. J. PROGAR  
GRANT #NAG-1-343

from

Chemistry Department  
Virginia Polytechnic Institute and State University  
Blacksburg, VA 24061  
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FIBER REINFORCED COMPOSITES  
-COMPOSITE MATERIALS  
THERMOPLASTICITY  
CHEMICAL BONDS  
FRACTURE STRENGTH

1

## INTRODUCTION

POLYMERIZATION  
THERMOSETTING RESINS  
VISCOSITY  
SURFACE FINISHING  
SIZING (SURFACE TREATMENT)  
MORPHOLOGY  
CARBON FIBERS  
X RAY SPECTROSCOPY

Thermoplastic matrices used for composites do not undergo polymerization reaction after being incorporated into the composite as thermosetting resins do. This fact leads to several consequences. The first is that thermoplastics will be less likely to form chemical bonds with the fiber. Another is that these thermoplastics will have a much higher viscosity when melted to apply them to the fiber than the thermoset monomers (oligomers). Thus, it will be much more difficult to obtain contact between fiber and matrix.

The interphase between fiber and matrix can have a large influence on the mechanical properties of composites. The properties of this interphase can be controlled by surface treating the fibers and by sizing the fiber. Surface treatment can change the functionality of the fiber surface as well as its morphology. Sizing typically consists either of a reactive low molecular weight compound, or else a dilute solution of a thermoplastic resin. The reactive groups on the low molecular weight compound are chosen so that they can react with both the fiber surface and the matrix. The work reported here is aimed at studying the effect of the properties of the carbon fiber surface on the fiber/matrix interaction.

## EXPERIMENTAL

### Carbon Fibers

The fibers used in this study included Hercules AS-4 and AU-4, two types of Union Carbide T-300 one untreated and one surface treated but unsized.

### Surface Treatment

Surface treatments were performed on Hercules AU-4 carbon fibers. The treatments included anodization in 0.5M sodium hydroxide (0.5M NaOH) and 0.5M sulfuric acid (0.5M H<sub>2</sub>SO<sub>4</sub>) at 6 volts for 2 min. The current densities were approximately 3.3 and 4.8 amperes per square meter, respectively.

### X-ray Photoelectron Spectroscopy

The surfaces of the fibers were analysed by X-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer Phi 5300 electron spectrometer. The fibers were mounted on the instrument probe with silver paint.

### Wetting Force Measurement

The wetting force of carbon fibers were measured in five liquids of varying polar and dispersive components using a Perkin-Elmer TGA-2 microbalance. The fibers were glued to a wire hook with a cyanoacrylate adhesive. The hook was then placed on the microbalance and the liquid raised up to the wetting liquid. Six fibers were measured for each surface treatment and liquid. The liquids used were: water, ethylene glycol, formamide, methylene iodide, and bromonaphthalene. Polar and dispersive components of the fiber surface energy were determined using the technique described in the previous report(1).

### Breaking Strength

The breaking strength of the fibers were measured at 2.54 cm length. The fibers were glued across a 2.5 cm. hole in a paper tab. A cyanoacrylate adhesive was used as the adhesive. The paper tab was then mounted in a table model Instron with a 20 gm capacity load cell using alligator clips. The paper was burned away with a nichrome wire attached to a wall outlet rheostat set at about 10 volts. The fiber was then pulled in tension with a crosshead speed of 5 mm per minute. 20-30 fibers were broken for each fiber of

interest. Breaking strength was also measured as a function of length. The fibers were mounted in paper tabs similar to the ones described above except that they had either 12.5 mm or 6 mm holes in them.

#### Fiber Critical Length

To measure the interaction of the matrix with the fiber, a fiber critical length test was performed as described by Wadsworth and Spilling (2). In this test, an annealed (500°F, 30 min-oven cool) coupon (15 cm X 15 cm) of A1100 aluminum was coated with a 5 gm/100 ml solution of UDEL F1700 polysulfone in methylene chloride. Fibers were then individually placed on the coated aluminum spaced about 5 mm apart. The fibers were then coated with the 5 gm/100 ml solution. After the solvent was allowed to evaporate, the coupons, fiber, polymer system was annealed at 250°C in a vacuum oven for 12 hours. The coupons were cooled in the oven. After cooling, the coupons were cut into 2.5 cm X 15 cm strips and pulled in tension to 30% strain in an Instron testing machine. The broken fiber lengths were measured on a microscope with a micrometer stage.

### RESULTS AND DISCUSSION

#### X-Ray Photoelectron Spectroscopy

The XPS results are shown in Figure 1. This figure shows the carbon 1s photopeaks for each fiber. Also listed next to the photopeaks are the atomic percentages of elements detected. It can be seen that AS-4 has a higher nitrogen content than AU-4. It was shown in the previous report (1) that the AS-4 surface was rich in amine groups. This is most likely a result of the proprietary surface treatment. The surface treatment on the T-300 fiber increased the oxygen content. The functionality is thus due to oxygen containing compounds. The sulfuric acid anodization increased the oxygen

content of the AU-4 fiber. It can also be seen from the shape of the carbon peak that there seems to be more carbon in the higher oxidation states than the other treatments.

#### Wetting Force Measurements

The polar ( $\gamma_p$ ) and dispersive ( $\gamma_d$ ) components of the surface energy of the carbon fibers are listed in Table I. There is a lot of scatter in this data and it is doubted if any of the differences are statistically significant. The only conclusion that may be drawn is that the T-300 fibers appear to have a lower polar contribution to their surface energy.

#### Breaking Strength

The breaking strengths of several of the carbon fibers (length: 2.54 cm) listed in Table II. It can be seen from this that the surface treatments used are reducing the strength of the fiber slightly. The breaking strengths as a function of length are plotted in Figure 2. The means and standard deviations of each plotted point are tabulated in Table III. It appears that the AS-4 fiber increases in strength sharply at shorter lengths. The AU-4 increases less sharply. It should be noted that the AS-4 and AU-4 were obtained from different batches. The differences observed may result from this fact rather than from the effect of the surface treatment. The breaking strength of the Union Carbide fibers was independent of length. These effects are due to the density and distribution of flaws on the surface of and within the fiber. Care should be used in analysing these data since the standard deviations listed in Table III are rather large. In fact from these, no real significant differences can be observed. It is felt however that a distribution analysis of the breaking strengths will show that there are some differences.

### Fiber Critical Lengths

Carbon fibers normally break at around 5% strain. It would be expected that stretching to 30% strain would result in the fiber breaking once and then no further breaks observed since the stress cannot be transferred through a broken fiber. However, the matrix can transfer stress to the fiber. Measurement of the lengths of the broken fibers is thus a measure of the ability of the matrix to transfer stress to the fiber. One problem that arises in the analysis is that the strength of the fiber will also influence the length at which the fibers break. Since the fibers are breaking at around 0.25-0.5 mm, it would be necessary to know the breaking strength of the fibers at this short length.

The fiber critical lengths are tabulated in Table IV. There is apparently no difference between the AS-4 and AU-4. The surface treated fibers had a shorter fiber length indicating that there was stronger interfacial adhesion to these fibers. However, the strengths of these fibers have not been taken into consideration. Therefore, it cannot be concluded at this time that the surface treatments used did in fact promote adhesion to the fiber.

### SUMMARY

Carbon fibers were obtained from several manufacturers. Surface treatments were performed on these fibers by anodization. The surfaces of these fibers were analysed by XPS and wetting force measurement. The breaking strength of these fibers was measured at 2.5 cm length. It was seen that the surface treatments reduces the strength of the fibers. It was also seen that the Hercules fibers had a higher breaking strength than the Union Carbide fibers. Fiber critical length measurements showed no difference in

critical lengths between AS-4 and AU-4 fibers embedded in polysulfone. However, the fiber lengths were much shorter for the surface treated fibers. This effect could be related to increased adhesion between fiber and matrix, or it could be due to the lower breaking strength of the surface treated fiber.

#### REFERENCES

- 1) DeVilbiss, T. A. and Wightman, J. P., "Fracture Surface Analysis in Composite and Titanium Bonding", Grant #NAG-1-343, September (1985).
- 2) Wadsworth, N. J. and Spilling, I., "Load Transfer from Broken Fibers in Composite Materials", Brit. J. Appld. Phys. (J. Phys. D) ser. 2, 1, 1049 (1968).



TABLE I  
SURFACE ENERGY ANALYSIS

Fiber	$\gamma_p$	$\gamma_d$
Celion 6000	18.1	29.6
AS-4	22.0	29.4
AU-4	18.2	28.1
NaOH Anodized	21.0	28.8
H <sub>2</sub> SO <sub>4</sub> Anodized	22.4	33.7
HNO <sub>3</sub> Boiled	18.1	29.6
T-300 No Shear	9.5	32.9
T-300 Shear	11.1	35.8

TABLE II  
BREAKING STRENGTH OF CARBON FIBERS

Fiber	S (GPa)	$\sigma$
Celion 6000	2.48	0.51
AS-4	2.87	0.87
AU-4	2.71	0.79
NaOH Anodized	2.21	0.78
H <sub>2</sub> SO <sub>4</sub>	2.12	0.95
T-300 No Shear	2.20	0.39
T-300 Shear	2.24	0.38

2.54 cm length

TABLE III

MEAN BREAKING STRENGTH ( $\bar{X}$ ) AND STANDARD DEVIATION ( $\sigma$ ) OF  
CARBON FIBERS AT VARIOUS LENGTHS

Fiber	2.54 cm		1.27 c		0.63 cm	
	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$	$\bar{X}$	$\sigma$
AS-4	14.7	4.5	16.7	3.1	20.4	3.2
AU-4	13.9	4.1	16.1	3.1	17.1	3.3
T-300	11.3	2.0	10.8	2.7	13.6	2.4
T-300 shear	11.5	1.9	11.4	2.9	12.8	3.0

TABLE IV

FIBER CRITICAL LENGTHS OF FIBERS CAST IN 5% UDEL P1700

Fiber	Fiber Length (mm)	$\sigma$
AS-4	0.45	0.12
AU-4	0.42	0.11
H <sub>2</sub> SO <sub>4</sub> Anodized	0.27	0.07
NaOH Anodized	0.34	0.08

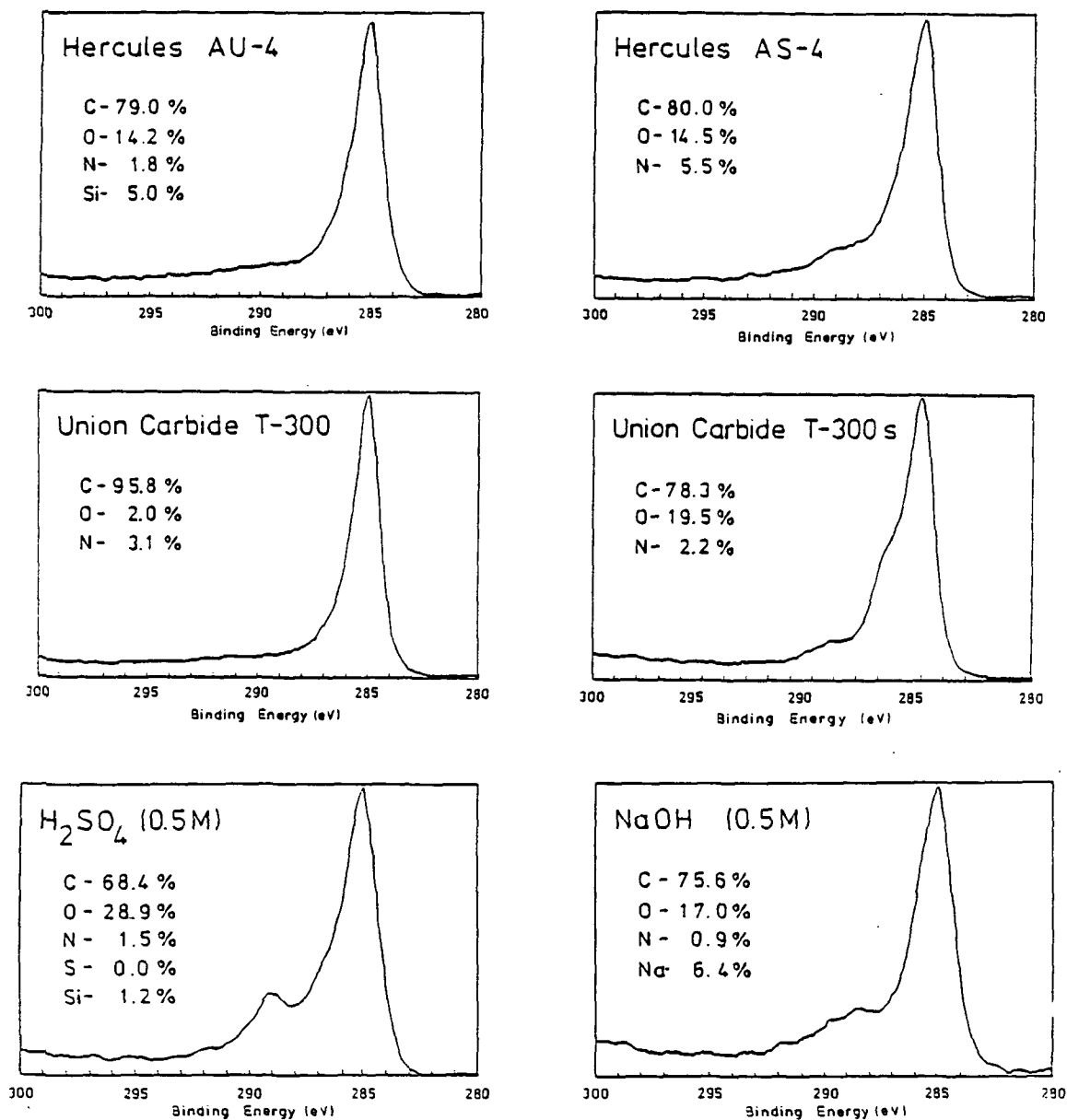


Figure 1. XPS C 1s photopeak of commercially available and anodized carbon fibers.

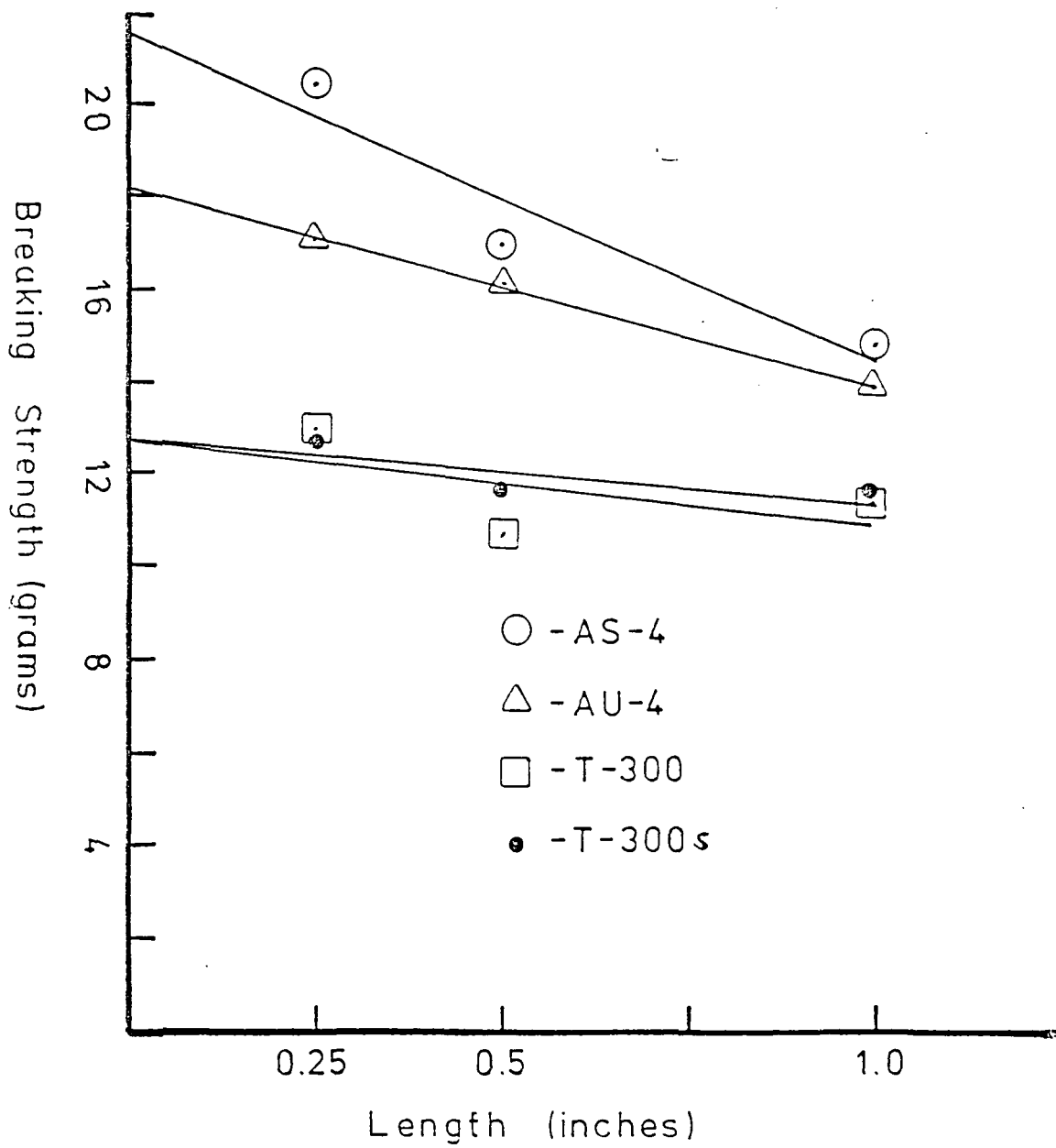


Figure 2. Breaking strength versus length of carbon fibers.